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Chemical Oxidation as a Stage of Highly Efficient Technologies for Textile Wastewater Treatment

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Abstract
The aim of the study was to determine the biological degradability of pollutants in textile wastewater exposed to the action of various oxidants used either separately or in different combinations. The oxidising agents were ozone, hydrogen peroxide and UV radiation. Researches were carried out using textile wastewater of different concentrations and compositions, including concentrated washing and dye baths, general averaged process wastewater and washing wastewater. It was found that oxidation processes appeared to be the most efficient methods for degradation of organic compounds present in wastewater. This was confirmed by decreasing COD values. However, in the case of BOD it was not so obvious. On the one hand, we could observe a decrease in its value, which was evidence of the decomposition of biodegradable organic compounds exposed to oxidation processes, but on the other, in many cases an increase in BOD was reported, which provided evidence of the degradation of organic compounds that were difficult to degrade biologically and of formation of more biodegradable compounds. It follows from the researches that ozone is the oxidizing agent which ensures the greatest increase in wastewater biodegradability. Special attention should be given to the selection of its proper doses.

Key words: *chemical oxidation, ozone, hydrogen peroxide, UV light, biodegradability.*

Introduction

One of the serious hazards for both surface and underground water are industrial wastewaters, including textile wastewater. The large quantities of wastewaters produced, their diversified composition, substantial load of organic and mineral pollutants, high toxicity and poor biodegradability cause that textile wastewater is one of the most difficult to treat. For these reasons it requires multistage treatment technology where after mechanical pretreatment, various physical, physicochemical, chemical and biological processes are applied. The proper selection and combination of subsequent stages of the treatment, taking into account the amount and specific features of the wastewater treated, enable the removal of pollutants with possible low investment and operation costs.

Recently, growing interest has been observed in multi-stage wastewater treatment technologies which include chemical oxidation processes and the so-called advanced oxidation processes (AOP) as one of the processing elements [1 - 3]. Many versions of these processes are known, their mutual feature being the formation of hydroxyl radicals with a high oxidizing potential, as well as their use in the oxidation of pollutants present in water [4]. HO· radials are generated in different ways, including the reaction of ozone with water, photolysis, hydrogen peroxide, Fenton reaction, photocatalysis with the use of titanium dioxide, radiation, etc. A detailed discussion of these processes can be found in survey articles and monographs [5 - 10].

The high reactivity of hydroxyl radicals and their low selectivity enable the oxidation of big groups of organic compounds present in textile wastewater, including dyes and detergents. At the same time this method can be used for wastewater with different compositions and concentrations of pollutants, which are characteristic of textile wastewater. An additional advantage of the method is that it does not cause secondary pollution of the environment and brings no risk of overdosing on oxidants. Oxidation reactions usually have a chain character which ensures high yield and rate of the process.

Advanced oxidation processes find multiple applications in textile wastewater treatment. Investigations were carried out on model objects, including solutions of dyes and detergents, as well as dye and washing baths [11 - 14]. Much attention was given to real textile wastewaters coming from factories which process a variety of natural and synthetic materials from different production cycles [15, 16]. Many versions of advanced oxidation processes were studied, including ozonation [12, 15, 17], the Fenton reaction [18], as well as processes involving hydrogen peroxide, UV light [3, 14, 16, 17], radiation [19] and photocatalytic processes [20]. The investigations confirmed that practically all versions of the oxidation processes efficiently reduce pollutants contained in the wastewater. The degrees of COD and TOC reduction obtained were high, and detergents, dyes and other organic components of the wastewater were almost completely removed. However, in most cases such deep oxidation of organic compounds in textile wastewater appeared to be not cost-effective. Partial chemical decomposition of pollutants is often sufficient, and the wastewater can be further processed easily using less expensive biological methods. The integration of chemical pretreatment with final treatment using biological processes is of great interest [21, 22].

Hence, the aim of our researches was to determine the biological degradability of pollutants present in textile wastewater exposed to a variety of oxidising agents used either separately or in different combinations. The oxidising agents were ozone, hydrogen peroxide and UV radiation. Experiments were carried out on textile wastewater of various concentrations and compositions including concentrated washing and dye baths, general

averaged process wastewater and rinsing wastewater. Conclusions drawn from the experiments are of great practical significance for potential industrial applications of the chemical oxidation methods.

Methodology

The material tested was wastewater of different concentration and composition produced in textile factories in Lodz:

- dye wastewater from the cotton dyeing process (samples 1, 2, 3, 4 and 10),
- dye wastewater from the polyester dyeing process (samples 5 and 6),
- washing wastewater (sample 7),
- averaged process wastewater (samples 8 and 9).

Initial values of COD and BOD_5 of the wastewater tested are given in Tables presenting experimental results.

The textile wastewater was processed using the following oxidising agents:

- ozone,
- hydrogen peroxide,
- ultraviolet light in the presence of oxygen,
- ozone combined with hydrogen peroxide,
- ozone used jointly with UV light,
- combined use of ozone, hydrogen peroxide and UV light.

In the ozonation experiments the system for wastewater processing was composed of the following elements: an ozonator with auxiliary equipment, a reaction vessel and a system of sorption washers. Oxygen was pressed from a steel cylinder to the ozonator through two drying columns filled with $CaCl_2$ and P_2O_5 deposited on glass packing, and next through a flowmeter used to read the oxygen flow velocity. The ozonator system contained an ELIMP device to measure ozone concentration, which allowed us to measure the content of ozone in oxygen at the reactor inlet and outlet. 1.3 dm^3 of wastewater was put in a glass reactor 1.5 dm^3 in volume equipped with a thermostating jacket. Oxygen with ozone flowing to the reactor was supplied to the solution by means of a porous plate which ensured good disintegration of the gas.

In the experiments with hydrogen peroxide, a 1.3 dm^3 sample of wastewater was placed in a thermostated reactor, and next the desired amount of H_2O_2 in the form of 30% solution was added. The reaction was continued for 8 hours. After completion of the process, unreacted hydrogen peroxide was decomposed using manganese dioxide.

The process of UV irradiation of the wastewater was carried out in a glass reactor with a quartz tube placed in the middle. In the tube there was an UV Q-400 burner connected to a system which supplied a lamp. The burner was cooled by flowing air. Oxygen flowing through the solution caused the mixing and aeration of the wastewater.

In the experiments with ozonation in the presence of hydrogen peroxide, 1 dm^3 of wastewater was placed in the thermostated reactor, and next the desired amount of hydrogen peroxide in the form of 30% solution was added. Then the ozone generator was started, and the oxygen flow rate and ozone concentration produced were determined. The reaction was carried out for a specified period which determined the dose of ozone supplied to the wastewater. At the end of the reaction, when the ozonator was stopped, oxygen was passed through the solution for about 15 minutes to remove the unreacted O_3. Hydrogen peroxide was removed from the reaction medium by means of manganese dioxide.

When the action of ozone was combined with UV irradiation, the process was started by turning on the ozonator and UV light source located at the centre of the reactor at the same time. After completion of the reaction, oxygen was passed through the solution for about 15 minutes to remove the unreacted O_3.

When hydrogen peroxide and UV radiation were used jointly, a determined quantity of hydrogen peroxide was added to the wastewater, and the UV lamp was turned on. The solution was mixed by flowing oxygen. After some time the reaction was interrupted by turning on the UV lamp. The unreacted hydrogen peroxide was removed from the wastewater by manganese dioxide.

Table 1. *Changes in COD, BOD_5 and BOD_5/COD in textile wastewater caused by ozonation depending on ozone doses.*

Sample no.	Ozone dose, mg O_3/dm^3	COD, mg O_2/dm^3	BOD_5, mg O_2/dm^3	BOD_5/COD, –
1	0	440	47	0.11
	180	435	55	0.13
	365	435	38	0.09
	550	385	60	0.16
	730	345	34	0.10
2	0	620	150	0.24
	145	585	95	0.16
	430	565	100	0.18
	720	540	95	0.18
3	0	320	64	0.20
	985	220	20	0.09
	1970	135	14	0.10
4	0	120	<10	<0.08
	145	115	<10	<0.09
	430	81	<10	<0.12
	720	63	<10	<0.16
5	0	1310	75	0.06
	985	990	220	0.22
	1970	980	50	0.05
6	0	510	125	0.25
	450	500	60	0.12
	900	455	130	0.29
	1350	445	75	0.17
	1800	440	150	0.34
7	0	1460	28	0.02
	180	1460	25	0.02
	365	1370	32	0.02
	550	1370	30	0.02
	730	1260	35	0.03
	1300	1220	23	0.02
	1800	1220	50	0.04
8	0	430	70	0.16
	145	400	65	0.16
	430	375	80	0.21
	720	335	110	0.33
9	0	320	42	0.13
	490	190	19	0.10
	985	130	34	0.26
	1480	140	47	0.34
	1970	120	18	0.15

In the case of the combined action of ozone, hydrogen peroxide and UV radiation, after placing the wastewater samples in the reactor and adding a specified quantity of hydrogen peroxide solution, both the ozone generator and UV light source were turned on simultaneously. After finishing the reaction, oxygen was passed through the solution for about 15 minutes to remove the remaining O_3. The unreacted hydrogen peroxide was decomposed by manganese dioxide.

Crude and processed wastewater was subjected to analytical control which encompassed the determination of:

- chemical oxygen demand (COD),
- biochemical oxygen demand (BOD_5).

Additionally, the biodegradability of the wastewater was measured by the BOD_5/COD ratio. An increase or decrease in this parameter might provide evidence of a growth or reduction in wastewater biodegradability, respectively.

Results and discussion

Ozonation

Table 1 shows changes in the COD, BOD_5 and biodegradability of wastewater (BOD_5/COD ratio) in subsequent textile wastewater samples which were the result of ozonation depending on the doses of ozone applied.

Ozonation caused the decomposition of pollutants in the wastewater and a reduction in chemical oxygen demand by several to dozens of percent. An increase in the ozone dose in the initial phase of the reaction induced a significant improvement in the COD reduction. At higher ozone doses reaching 700 - 1000 mg O_3/dm^3 and more, the decrease in COD was much smaller. This could lead to a conclusion that only the compounds most resistant to oxidation remained in the solution.

In the case of BOD_5, a considerable variability of changes in this parameter was observed after the ozonation process. From among the four samples of wastewater from cotton dyeing tested, only in one was a distinct twofold increase in biodegradability found (sample 4). In the other samples subjected to ozone treatment, biodegradability was at a similar level to that of the initial wastewater, or even lower. In the wastewater from polyester dyeing, the ozone treatment resulted in increased biodegradability. In the case of washing wastewater at high loading and particularly high toxicity, no changes in biodegradability were observed despite the application of extremely large ozone doses. A remarkable growth in the BOD_5/COD ratio was reported during the ozonation of averaged process wastewater (sample 8).

In conclusion, no explicit generalisation can be made. The decomposition of pollutants in wastewater induced by ozone and their biodegradability primarily depends on the type of raw material and technologies currently used in the factory. For instance, in wastewater with almost identical initial values of COD and BOD_5 but from two different factories, in one sample a decrease in biodegradability was reported, while in the other there was an increase (samples 3 and 9).

When the effect of a dose of ozone on wastewater biodegradability was analysed depending on the initial COD value, no evident regularities were observed either. Both its increase and decrease were reported as being equal for the wastewater at low and high loading.

Hydrogen peroxide

Table 2 gives results of the reduction in the COD, BOD_5 and BOD_5/COD ratios for selected types of wastewater and different amounts of hydrogen peroxide added.

Results of the experiments show that the wastewater decomposition efficiency depended primarily on the type of wastewater and dose of hydrogen peroxide. The COD reduction was usually small, reaching several percent only. At high doses of hydrogen peroxide, it increased to dozens of percent. The fact that wastewater decomposition is the main factor influencing its treatment is confirmed by comparison of the effects of the decomposition of wastewaters with almost identical initial values of COD and BOD_5 (samples 3 and 9). In one sample a decrease in biodegradability was reported, while another showed a growth. From among the samples tested, only in general averaged process wastewater was there over a double increase in biodegradability observed. On the other hand, in all dyehouse wastewater the BOD_5/COD ratio was significantly reduced. As with ozonation, in the treatment with hydrogen peroxide no explicit relations were observed. In general it can be stated, however, that the use of big doses of hydrogen peroxide has no favorable effect on wastewater biodegradability.

UV radiation

Changes in COD, BOD_5 and BOD_5/COD in textile wastewater induced by UV irradiation are presented in ***Table 3***.

When photooxidation processes were used in the textile wastewater treatment, very different degrees of COD and BOD_5 reduction were observed depending mainly on the type of wastewater tested. In the case of the two wastewater samples from the dyeing of cotton (samples 3 and 10) and those from polyester (samples 5 and 6), in two cases an increase in biodegradability was found after UV treatment, while in the other two a decrease was observed. An increase in the BOD_5/COD ratio was obtained for averaged process wastewater (sample 9). When analysing

Table 2. *Changes in COD, BOD_5 and BOD/COD in textile wastewater caused by oxidation with hydrogen peroxide.*

Sample no.	H_2O_2 dose, cm^3/dm^3	COD, mg O_2/dm^3	BOD_5, mg O_2/dm^3	BOD_5/COD, –
3	0	320	64	0.20
	5	300	<10	<0.03
	10	290	33	0.11
5	0	1310	75	0.06
	5	1310	93	0.07
	10	1280	13	0.01
6	0	510	125	0.25
	1	510	85	0.17
	2	500	95	0.19
	3	490	65	0.13
	5	490	75	0.15
9	0	320	42	0.13
	5	210	54	0.26
	10	170	50	0.29
	15	170	49	0.29
	20	150	10	0.07
10	0	430	132	0.31
	0.5	430	77	0.18
	1.0	345	40	0.12
	1.5	320	15	0.05
	2.0	320	23	0.07

Table 3. *Changes in COD, BOD_5 and BOD_5/COD in textile wastewater caused by UV irradiation.*

Sample no.	Time, h	COD, mg O_2/dm^3	BOD_5, mg O_2/dm^3	BOD_5/COD, –
3	0	320	64	0.20
	1	185	15	0.08
	2	170	15	0.09
5	0	1310	75	0.06
	1	1080	78	0.07
	2	870	95	0.11
6	0	510	125	0.25
	0,5	450	50	0.11
	1	440	26	0.06
	1,5	425	40	0.09
	2	410	29	0.07
9	0	320	42	0.13
	1	150	26	0.17
	2	110	24	0.22
	6	150	27	0.18
10	0	430	132	0.31
	2	430	145	0.34
	5	430	130	0.30
	10	430	140	0.32
	15	430	185	0.43

Table 4. *Changes in COD, BOD_5 and BOD_5/COD in textile wastewater caused by the combined action of ozone and hydrogen peroxide depending on the O_3 and H_2O_2 dose.*

Sample no.	O_3 dose, mg O_3/dm^3	H_2O_2 dose, cm^3	COD, mg O_2/dm^3	BOD_5, mg O_2/dm^3	BOD_5/COD, –
3	0	0	320	64	0.2
	985	5	190	10	0.05
	1970	10	135	63	0.47
5	0	0	1310	75	0.06
	985	5	1310	73	0.06
	1970	10	1080	30	0.03
6	0	0	510	125	0.25
	900	1	415	70	0.17
	900	2	375	110	0.29
	900	3	400	115	0.29
	900	5	405	125	0.31
9	0	0	320	42	0.13
	900	5	130	13	0.1
	900	10	110	<10	<0.09
	900	20	175	<10	<0.06
10	0	0	430	132	0.31
	1800	0.5	200	55	0.28
	1800	1.0	185	16	0.09
	1800	1.5	145	60	0.41
	1800	2.0	115	20	0.17

Table 5. *Changes in COD, BOD_5 and BOD_5/COD in textile wastewater due to the combined action of ozone and UV radiation depending on the reaction time.*

Sample no.	O_3 dose mg O_3/dm^3	Time h	COD mg O_2/dm^3	BOD_5 mg O_2/dm^3	BOD_5/COD –
3	0	0	320	64	0.20
	985	1	140	10	0.07
	1970	2	125	13	0.10
9	0	0	320	42	0.13
	985	1	105	12	0.11
	1970	2	105	18	0.17
5	0	0	1310	75	0.06
	985	1	1020	40	0.04
	1970	2	960	75	0.08
10	0	0	430	132	0.31
	900	1	180	50	0.28
	1800	2	110	38	0.34
6	0	0	510	125	0.25
	900	1	440	74	0.17
	1800	2	340	89	0.26

the process of photooxidation in time, it appeared that in four samples out of five, a prolonged time, i.e. an increase in UV radiation, improved, sometimes slightly, the wastewater's biodegradability.

Combined action of ozone and hydrogen peroxide

Table 4 shows changes in COD, BOD_5 and BOD_5/COD in textile wastewater induced by combined treatment with ozone and hydrogen peroxide depending on the time and amount of H_2O_2.

Most of the pollutants contained in the textile wastewater subjected to combined treatment with ozone and hydrogen peroxide were decomposed. The degrees of reduction obtained depended on both the type of wastewater and on doses of the two oxidising agents. At a constant ozone dose and variable amount of hydrogen peroxide (samples 6, 9 and 10), the COD reduction degree increased considerably. In the case of wastewater from cotton dyeing (sample 10), by increasing the amount of H_2O_2 from 0.5 cm^3 to 2 cm^3 (i.e. using small doses), the COD reduction increased from 54% to 73%. The wastewater from polyester dyeing (sample 6) behaved in an opposite way: with an increase in the quantity of hydrogen peroxide added, the reduction was increased very slightly from 19 to 21%. From the point of view of biodegradability, the most favorable seems to be a simultaneous increase in the doses of the two oxidants (samples 3 and 5). For sample 3, a multiple increase in biodegradability was obtained. An optimal selection of doses of both oxidants which ensures a significant growth in wastewater biodegradability depends primarily on the type and character of the wastewater treated and should be settled individually.

Combined action of ozone and UV radiation

Table 5 shows changes in COD, BOD_5 and BOD_5/COD in textile wastewater which are a result of the combined action of ozone and UV radiation.

The results show the evident effect of ozonation combined with UV irradiation. The degrees of COD reduction increased from 27% (sample 5) to 75% (sample 10). The changes in wastewater biodegradability were usually insubstantial. A noticeable decrease was observed in sample 3, while there was an increase in sample 9.

Combined action of hydrogen peroxide and UV radiation

Changes in COD, BOD_5 and BOD_5/COD in textile wastewater caused by the combined action of UV radiation and hydrogen peroxide are shown in ***Table 6***.

The COD reduction and changes in biodegradability were analysed in relation to the reaction time and quantity of hydrogen peroxide applied. Despite the short reaction time for the averaged process wastewater (sample 9) at big doses of hydrogen peroxide, significant degrees of COD reduction were obtained. Furthermore, in the case of wastewater from polyester dyeing (sample 6) for a prolonged reaction time of 2 hours with five times smaller doses of H_2O_2, the COD reduction was high – 45%. Much more resistant to oxidation processes appeared to be another type of highly concentrated wastewater from polyester dyeing (sample 5) where COD reduction did not exceed several percent. In most cases a distinct or slight increase in biodegradability was observed. Only in sample 3 at high reaction degrees was the BOD_5/COD ratio reduced.

Combined action of ozone, hydrogen peroxide and UV radiation

Changes in COD, BOD_5 and BOD_5/COD in textile wastewater caused by the combined action of ozone, UV radiation and hydrogen peroxide are shown in ***Table 7***.

In the case of combined ozonation, hydrogen peroxide and the UV irradiation of wastewater, very good results were obtained with respect to pollutant reduction. This can be observed particularly in the averaged process wastewater (sample 9), where COD reduction was 94% and in the cotton dyeing wastewater (sample 10) with 87% reduction. Moreover, highly concentrated polyester dyeing wastewater (sample 5) was well degraded after a not very long reaction time and small doses of O_3 and H_2O_2. A significant increase of biodegradability was reported. A decrease was observed only at high reaction degrees (sample 10).

Diversity and continual changes in the composition and quantity of wastewater generated in textile factories make treatment processes difficult. The methods proposed should be efficient, economical and flexible. The installation should be prepared for frequent changes in treatment methods and big variability in the wastewater residence times. Advanced oxidation processes are characterised by high flexibility and, consequently, a significant ability to change oxidation parameters. The changing and selection of reagent doses for such substrates as ozone or hydrogen peroxide is a simple task. Changing the reaction time is not troublesome either, provided the installation is equipped with sufficiently large tanks. Proper selection of parameters for treatment processes requires continuous control of the parameters of crude and treated wastewater.

In most cases advanced oxidation processes are efficient in the decomposition of pollutants contained in textile wastewater. Ozonation and different versions of combined treatment with ozone, hydrogen peroxide and UV radiation cause a significant decrease in initial COD values, exceeding even 90% (cf. sample 9, combined action of O_3, H_2O_2 and UV). Worse results were obtained when hydrogen peroxide or photooxidation was used. Although the photooxidation lasted for 15 hours, no COD reduction was

Table 6. *Changes in COD, BOD_5 and BOD_5/COD in textile wastewater caused by the combined action of UV radiation and hydrogen peroxide depending on the reaction time and H_2O_2 dose.*

Sample no.	Time, h	H_2O_2 dose, cm^3	COD, mg O_2/dm^3	BOD_5, mg O_2/dm^3	BOD_5/COD, -
3	0	0	320	64	0.20
	1	5	125	42	0.34
	2	10	180	<10	0.06
5	0	0	1310	75	0.06
	1	5	1230	107	0.09
	2	10	1280	127	0.10
6	0	0	510	125	0.25
	2	1	465	57	0.12
	2	2	390	95	0.24
	2	3	355	93	0.26
	2	5	330	96	0.29
9	0	0	320	42	0.13
	1	5	275	17	0.06
	1	10	200	<10	0.05
	1	15	244	<10	0.07
	1	20	230	18	0.14
	1	25	42	<10	0.24

Table 7. *Changes in COD, BOD_5 and BOD_5/COD in textile wastewater caused by the combined action of ozone, UV irradiation and hydrogen peroxide depending on the reaction time and H_2O_2 dose.*

Sample no.	O_3 dose mg O_3/dm^3	Time h	H_2O_2 dose cm^3	COD mg O_2/dm^3	BOD_5 mg O_2/dm^3	BOD_5/COD –
3	0	0	0	320	64	0.20
	985	1	5	175	72	0.41
	1970	2	10	245	11	0.04
5	0	0	0	1310	75	0.06
	985	1	5	1000	235	0.23
	1970	2	10	780	84	0.11
6	0	0	0	510	125	0.25
	900	1	1	395	110	0.28
	900	1	2	370	90	0.24
	900	1	3	375	100	0.27
	900	1	5	340	160	0.47
9	0	0	0	320	42	0.13
	985	1	5	32	<10	<0.31
	985	1	10	70	<10	<0.14
	985	1	15	<20	<10	<0.27
	985	1	20	<20	<10	<0.47
10	0	0	0	430	132	0.31
	1800	2	0,5	255	185	0.72
	1800	2	1	110	40	0.36
	1800	2	1,5	95	33	0.35
	1800	2	2	58	<10	0.17

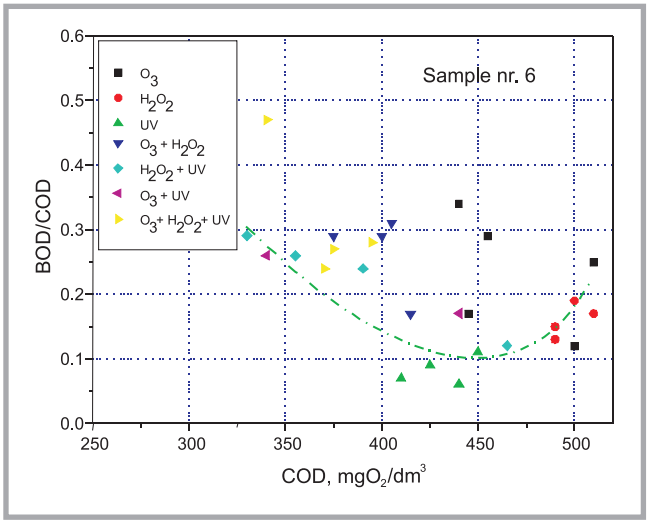

Figure 1. *Dependence of biodegradability (BOD_5/COD) on the COD value obtained by various methods of advanced oxidation for polyester dyeing wastewater (sample 6).*

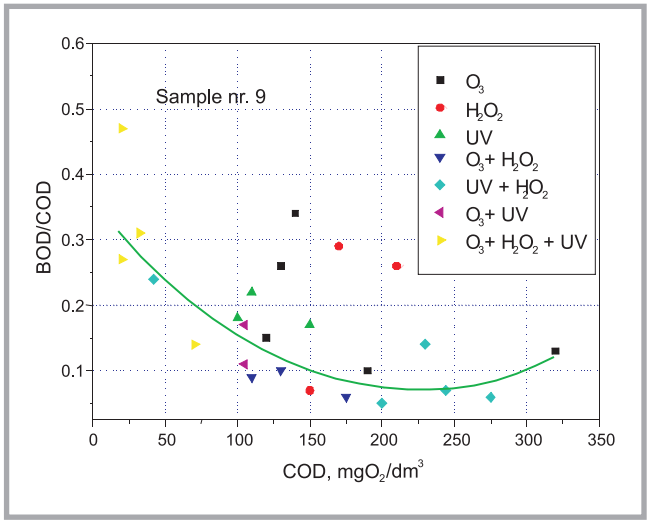

Figure 2. *Dependence of biodegradability (BOD_5/COD) on the COD value obtained using different versions of advanced oxidation for averaged process wastewater (sample 9).*

observed for sample 10. Poor effects of COD reduction with the use of hydrogen peroxide were obtained for samples 3, 6 and 5 despite the application of big doses of H_2O_2.

Advanced oxidation processes have a diverse effect on wastewater biodegradability measured by the BOD_5/COD ratio. These relations depend not only on the wastewater type and composition but also on the method of treatment applied and the amount of oxidants used. This is clearly reflected by the relations between the biodegradability (BOD_5/COD) and COD values of wastewater subjected to the different versions of advanced oxidation processes shown in ***Figures 1*** and ***2*** for polyester dyeing wastewater (sample 6) and averaged process wastewater (sample 9).

Based on the results shown in ***Figures 1*** and ***2***, it can be concluded that the mechanism of pollutant decomposition in wastewater in certain AOP versions is similar. For instance, in sample 6, the products of pollutant oxidation formed in processes induced by hydrogen peroxide, UV radiation and the combined action of these agents are probably identical, and the specified dependence of biodegradability on the COD of the wastewater can be determined, as shown by the curve in the graph below. The process of ozonation, the combined action of ozone and hydrogen peroxide as well as ozone, hydrogen peroxide and UV radiation probably proceed according to different mechanisms resulting in the formation of other products of pollutant decomposition. This is reflected by significant deviations from the relations determined by the curve in the graph. Comparison of results for other wastewater samples tested confirms that the method of treatment has a significant effect on biodegradability.

Selection of the most advantageous version of AOP for textile wastewater treatment which ensures satisfactory biodegradability depends, on the one hand, on the type and composition of the wastewater, and on the other on the selected combination and doses of oxidants applied. Each time this requires a precise analysis of the wastewater composition, which may be somewhat troublesome and difficult. For these reasons, it is easier to compare the reduction degrees of the basic parameters of the wastewater for similar reaction times. ***Figure 3*** shows COD values for different versions of advanced oxidation processes. Based on these data, it is easier to estimate the desirable degree of wastewater treatment with the use of biological methods.

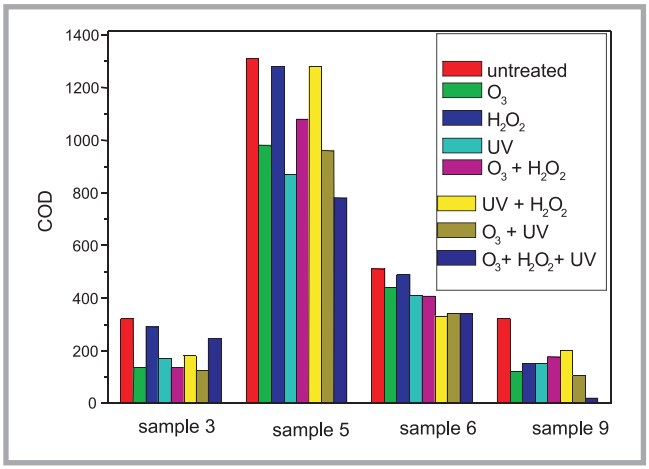

Figure 3. *Changes in wastewater COD for various types of chemical oxidation.*

Concluding remarks

In summary, the processes of oxidation with the use ozone, hydrogen peroxide and UV radiation constitute efficient methods for the decomposition of organic compounds present in wastewaters, which is confirmed by a decreasing wastewater COD. The situation is not so unambiguous in the case of wastewater BOD. On the one hand, we can observe a decrease in BOD, which is evidence of the decomposition of biodegradable organic compounds induced by oxidation processes. On the other hand, in many cases an increase in BOD is reported, which shows a proceeding decomposition of hardly biodegradable organic compounds and the formation of more biodegradable compounds.

A result of the correlation between COD and BOD_5 in the wastewater is the BOD_5

to COD ratio, which is a measure of wastewater biodegradability. In wastewater subjected to oxidation, increasing, decreasing and stagnant values of this parameter are reported as being equal. It seems that the correlations observed can be explained in the following way: when the parameter increases, the decomposition of hardly biodegradable organic compounds most probably proceeds with better efficiency as compared to the simultaneous oxidation and decomposition of easily biodegradable compounds. When this parameter decreases, the situation is opposite, i.e. the oxidation of non-biodegradable organic compounds is less efficient compared to the simultaneous oxidation and decomposition of easily biodegradable compounds. In cases where wastewater biodegradability remains invariable, the efficiency of the oxidation of biodegradable organic compounds is balanced by their formation in the processes of the oxidation and decomposition of hardly biodegradable compounds.

Changes in wastewater biodegradability depended directly on the type and dose of oxidants used. Among the oxidizing agents applied (ozone, hydrogen peroxide and UV radiation), ozone appeared to be the strongest oxidant, while UV light was the weakest.

In the case of ozone application, with an increase in its dose, a decrease in wastewater biodegradability was usually observed, which resulted from the high oxidising potential of ozone. In the proceeding reactions the quick non-selective decomposition of both easily and hardly biodegradable compounds was observed. This was revealed by a distinct decrease in the wastewater COD , and by a BOD_5 which remained at a similar level. In some types of wastewater (washing wastewater, general averaged process wastewater) particularly susceptible to oxidation with ozone, when the COD decrease was especially high (by 50-70%), a remarkable, even twofold or threefold increase in wastewater biodegradability was observed, which was probably due to the efficient decomposition of complicated organic structures into simpler, more biodegradable ones.

When hydrogen peroxide was used, the biodegradability of the wastewater noticeably diminished. This was primarily a result of the much weaker oxidising properties of hydrogen peroxide, which was shown by a slight decrease in COD in the wastewater treated, reaching several percent at most. At the same time, the reduction in wastewater BOD_5 was considerable. Hence, in actual fact hydrogen peroxide induced the decomposition of well biodegradable compounds only. This caused a decrease in the overall susceptibility of the wastewater to biological degradation.

In the case of UV light application, in most samples, with prolonged exposure to UV, wastewater biodegradability decreased. A slight reduction in COD was reported at a significant decrease in the wastewater's BOD_5 , which proved the domination of the oxidation of easily biodegradable compounds over the oxidation of hardly biodegradable ones. In some of the samples, wastewater biodegradability increased remarkably, especially those in which UV irradiation induced a significant decrease in COD with BOD_5 remaining at a constant or slightly increasing level. In this case there was an efficient decomposition of hardly biodegradable compounds.

It follows from the tests that ozone is an oxidant which induces the most significant increase in wastewater biodegradability. However, its dose should be determined very carefully.

References

1. *Beltran F. J., Gonzales J., Industrial wastewater advanced oxidation. Part 1. UV radiation in presence and absence of hydrogen peroxide, Water Research, 31, 2405-2414, 1997.*
2. *Beltran F. J., Encinar L., Gonzales J., Industrial wastewater advanced oxidation. Part 2. Ozone combined with hydrogen peroxide or UV radiation, Water Research, 31, 2415-2428, 1997.*
3. *Kos L., Perkowski J., Ledakowicz S., Application of ozone, hydrogen peroxide and UV irradiation in textile wastewater treatment, AATCC Review, 4 (1), 30-34, 2004.*
4. *Rice R.G., Applications of ozone for industrial wastewater treatment – a review, Ozone Science & Engineering, 19(5), 477, 1997.*
5. *Getoff N., Radiation-induced degradation of water pollutants – state of the art, Radiation Physical Chemistry, 47 (4), 581-593, 1996.*
6. *Getoff N., Advancements of radiation-induced degradation of pollutants in drinking and wastewater, International Journal Applied Radiation and Isotopes, 40, 585, 1998.*
7. *Andreozzi R., Caprio V., Isola A., Marotta R., Advanced Oxidation Processes (AOP) for water purification and recovery, Catalysis Today, 53, 51-59, 1999.*
8. *Malato S., Blanco J., Vidal A., Richter C., Photolysis with solar energy at a pilot plant scale: an overview, Appl. Cat. B. Ener., 37, 1-15, 2002.*
9. *Fasnacht M.P., Blough N.V., Aqueous photodegradation of polycyclic aromatic hydrocarbons, Environ. Sci. Technol., 36, 4361-4369, 2002.*
10. *Goi A., Trapido M., Hydrogen peroxide, Fenton reagent and photo-Fenton for the degradation of nitrophenols: a comparative study, Chemosphere, 46, 913-922, 2002.*
11. *Perkowski J., Kos L., Żyłła R., Ledakowicz S., A kinetic model of decoloration of water solutions of anthraquinone dye initiated by generality hydroxyl radicals, Fibres & Textiles in Eastern Europe, 54 (6), 59-64, 2005.*
12. *Bulska A., Perkowski J., Kos L., The application of ozone in the decomposition of aqueous solution of nonionic surfactants, Ozone Science & Engineering, 26 (2), 217-226, 2004.*
13. *Perkowski J., Mayer J., Kos L., Reactions of non-ionic surfactants, Triton X-n type, with OH radicals. A review, Fibres & Textiles in Eastern Europe, 50 (2), 81-85, 2005.*
14. *Perkowski J., Kos L., Decoloration of model dyehouse wastewater with advanced oxidation processes, Fibres & Textiles in Eastern Europe, 41 (2), 88-94, 2003.*
15. *Perkowski J., Kos L., Ledakowicz S., Application of ozone in textile wastewater treatment, Ozone Science & Engineering, 18 (1), 73-85, 1996.*
16. *Kos L., Perkowski J., Decoloration of real textile wastewater with advances oxidation processes, Fibres & Textiles in Eastern Europe, 43 (4), 81-85, 2003.*
17. *Perkowski, J., Kos, L., Ledakowicz, S., Advanced oxidation of textile wastewaters, Ozone Science & Engineering, 22, 535-550, 2000.*
18. *Perkowski J., Jóźwiak W., Kos L., Stajszczyk P., Application of Fenton's reagent in detergent separation in highly concentrated water solutions, Fibres & Textiles in Eastern Europe, 59(5), 114-119, 2006.*
19. *Perkowski, J., Kos L., Gamma irradiation combined with ozonization as a method of decomposition of impurities in textile wastes, Environ. Protec. Eng., 18, 5-17, 1992.*
20. *Kos L., Perkowski J., Bzdon S., Application of photocatalytic oxidation in the presence of TiO_2 in small sewage treatment plants, Separation Science and Technology, 42, 1553-1563, 2007.*
21. *Beltran F.J., Garcia-Araya J.F., Alvarez P., Impact of chemical oxidation on biological treatment of a primary municipal wastewater, Ozone Science & Engineering, 19, 513, 1997.*
22. *Scott J.P., Ollis D.F., Integration of chemical and biological oxidation processes for water treatment: review and recommendations, Environ. Progress, 10, 88, 1995.*

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